Electronic Supplementary Material (ESI) for Polymer Chemistry.

Electronic Supplementary Material

Elastomeric and pH-responsive hydrogels based on direct crosslinking of the poly(glycerol sebacate) pre-polymer and gelatin

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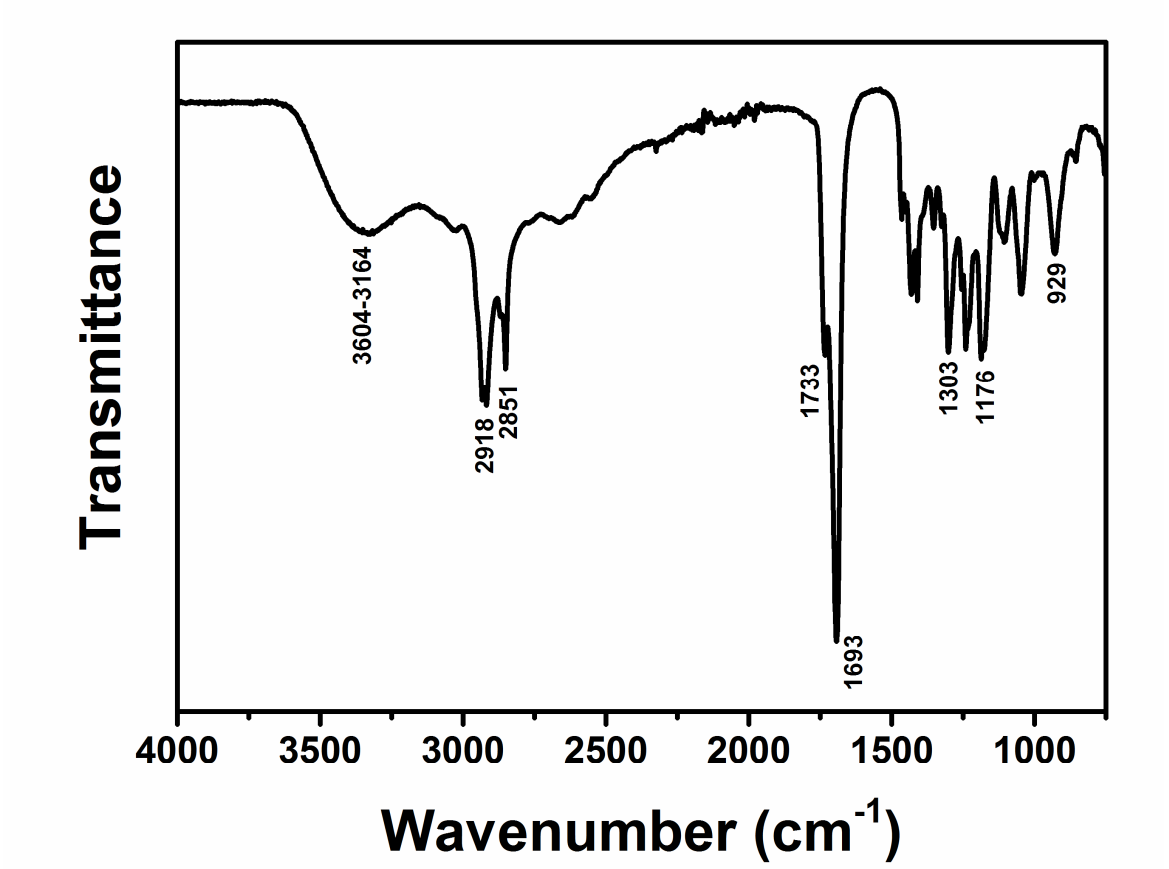

Fig. S1 FTIR spectrum of poly(glycerol sebacate) (PGS) pre-polymer before copolymerisation with gelatin. The broad band between 3604–3164 cm^{-1} is attributed to the hydroxyl groups (O–H), and the peaks at 2918 and 2851 cm^{-1} are for the stretching vibration of alkane groups ($–CH_2$).[1,2] Absorption of alkane groups is presented between 1354–1465 cm^{-1}.[3] The intense peak at 1733 cm^{-1} (C=O) and 1176 cm^{-1} (C–O) are the signature band of ester linkages.[2] The absorption peaks at 1693 cm^{-1} (dimer C=O), 1303 cm^{-1} (C–O stretching), and 929 cm^{-1} (O–H bending) are attributed to the carboxylic acid groups.[2]

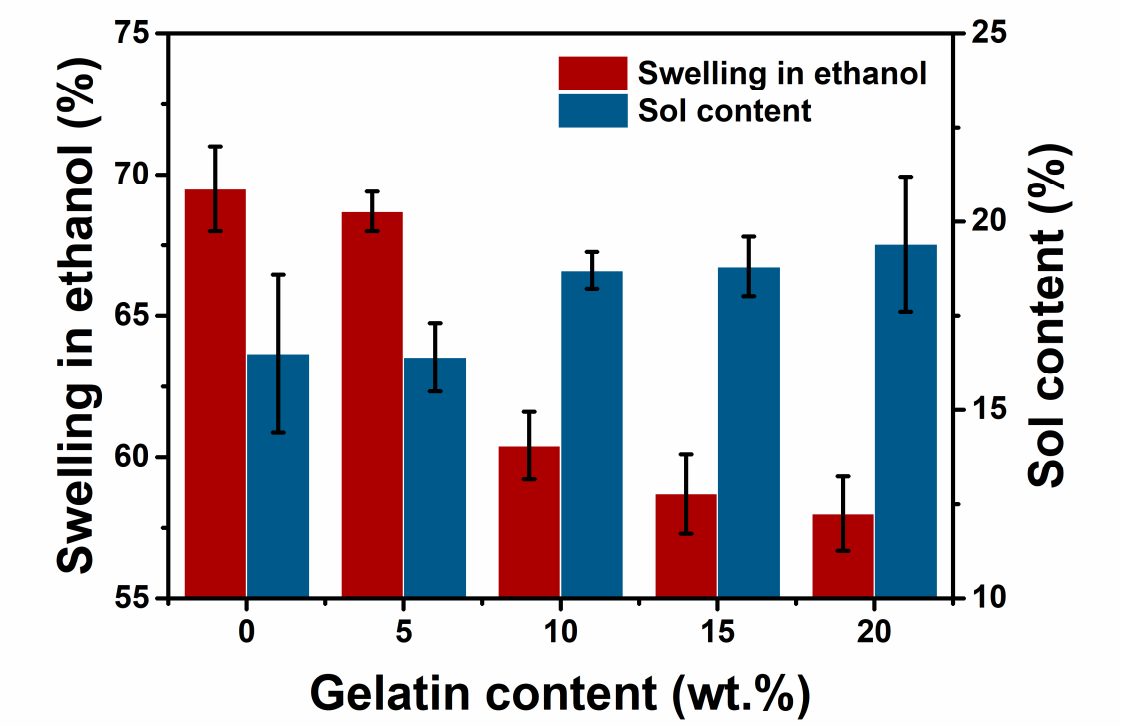

Fig. S2 The measured maximum ethanol uptake and weight loss after the sol extraction of poly(glycerol sebacate) and gelatin copolymer (PGSG) specimens.

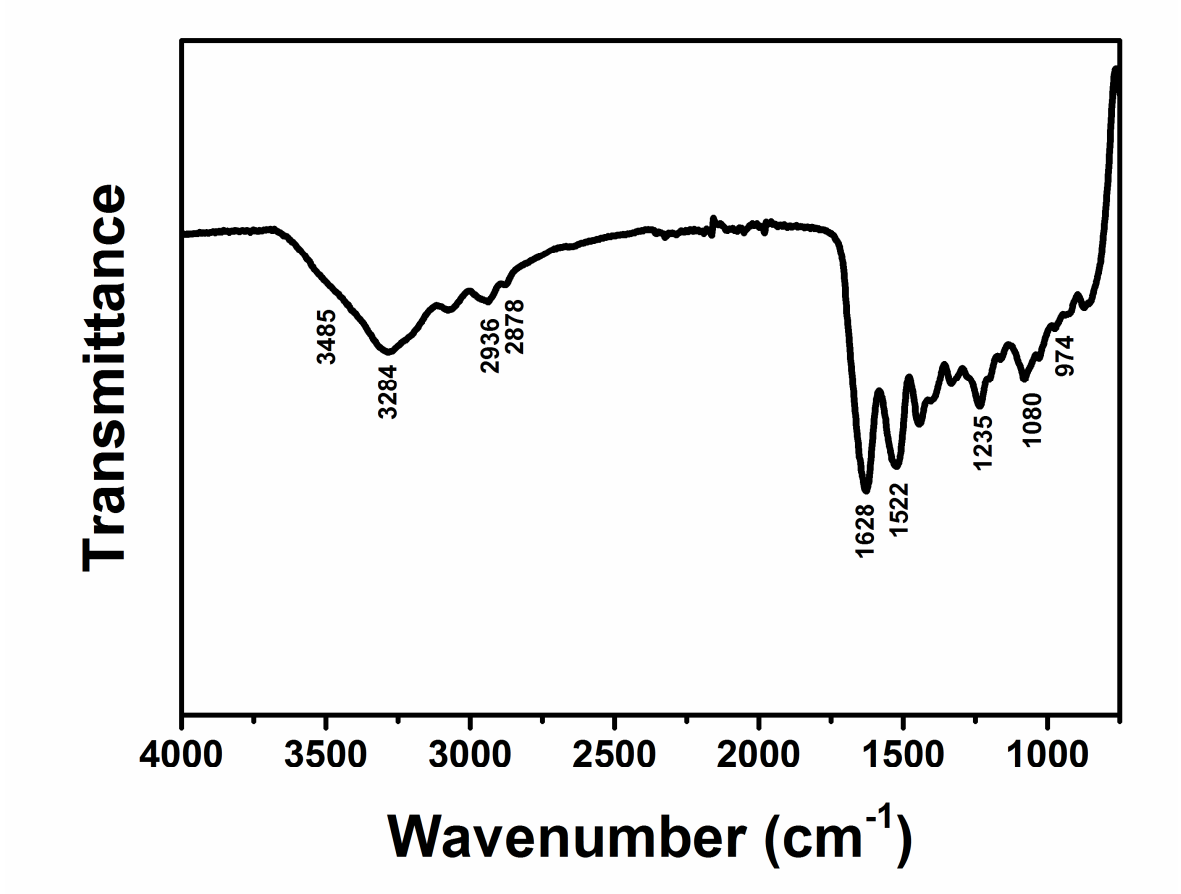

Fig. S3 FTIR spectrum of gelatin revealing a set of chemical functional groups such as amine, amide, hydroxyl, and carboxyl groups, derived from its abundant amino acid composition.[4–6] The broad band at 3485 cm^{-1} and 3284 cm^{-1} are attributed to the hydroxyl groups (O–H) and free amine groups (N–H stretching).[7] The amide peaks in gelatin backbones are identified as follows: amide I peak (C=O stretching) at 1628 cm^{-1}, amide II peak at 1522 cm^{-1} (N-H bending and C-H stretching), and amide III peak (C-N stretching and N-H in phase bending) at 1235 cm^{-1}.[8] The peaks at 2936 cm^{-1} and 2878 cm^{-1} are due to alkane groups (C–H stretching).[9] The peaks at 1080 cm^{-1} (C–O) and 974 cm^{-1} (O–H) are attributed to the carboxylic acid groups in gelatin.[4]

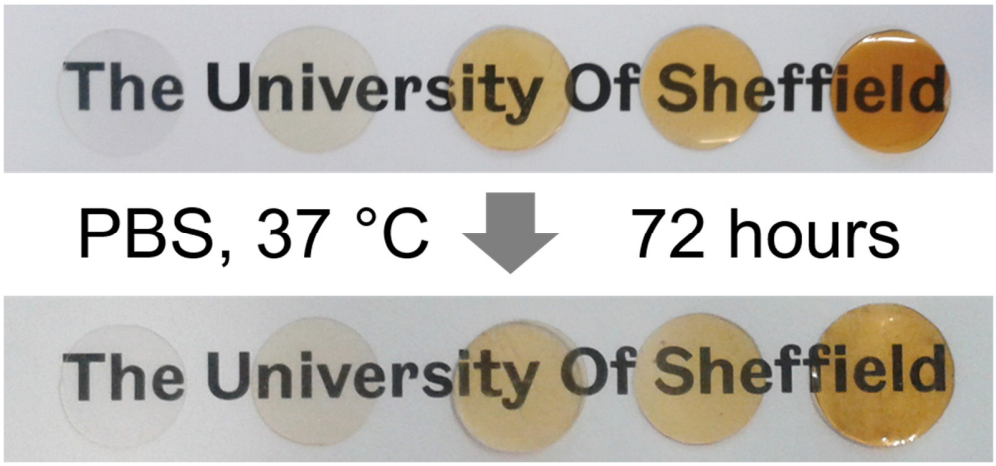

Fig. S4 Photographs of PGSG copolymers before and after swelling in phosphate buffered saline (PBS) for 72 h at 37 °C (from left to right PGSG0, PGSG5, PGSG10, PGSG15, and PGSG20), showing volume expansions.

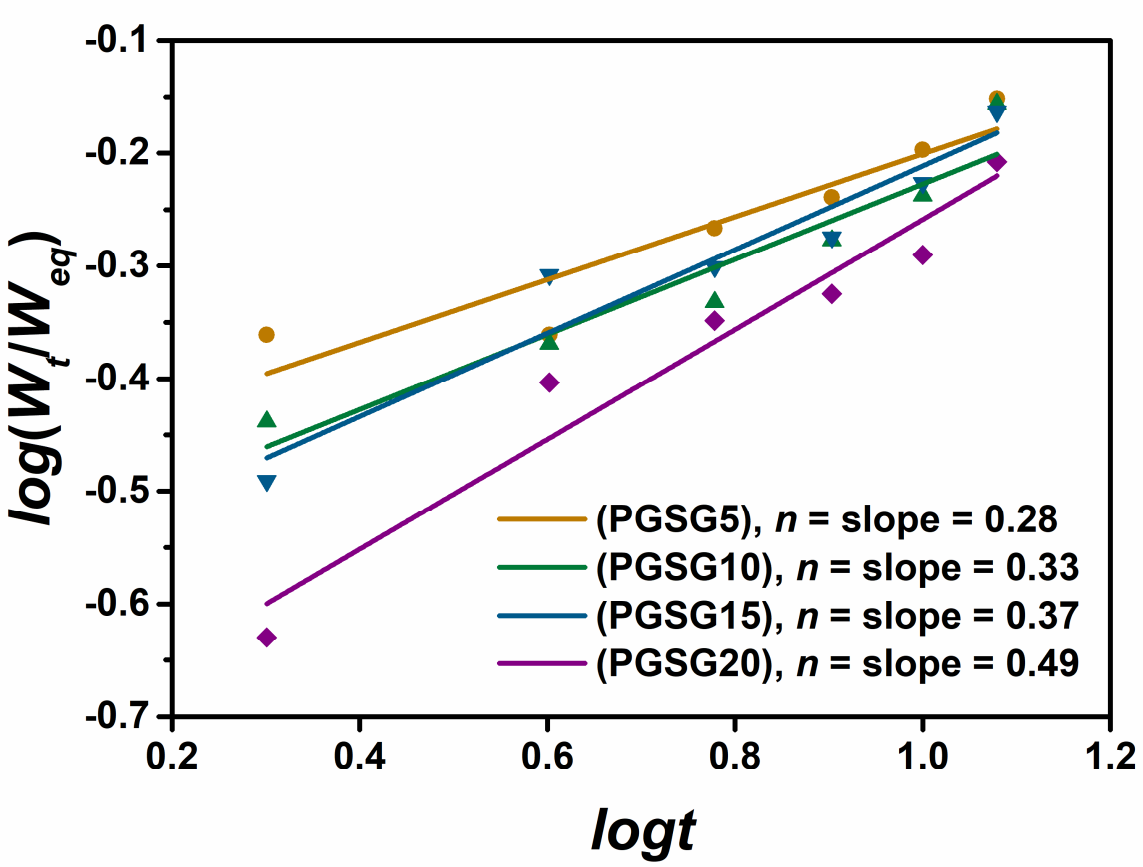

Fig. S5 The swelling ratio of PGSGs fit to Ritger-Peppas equation, with the *n* values shown by the slope of the fitting lines.

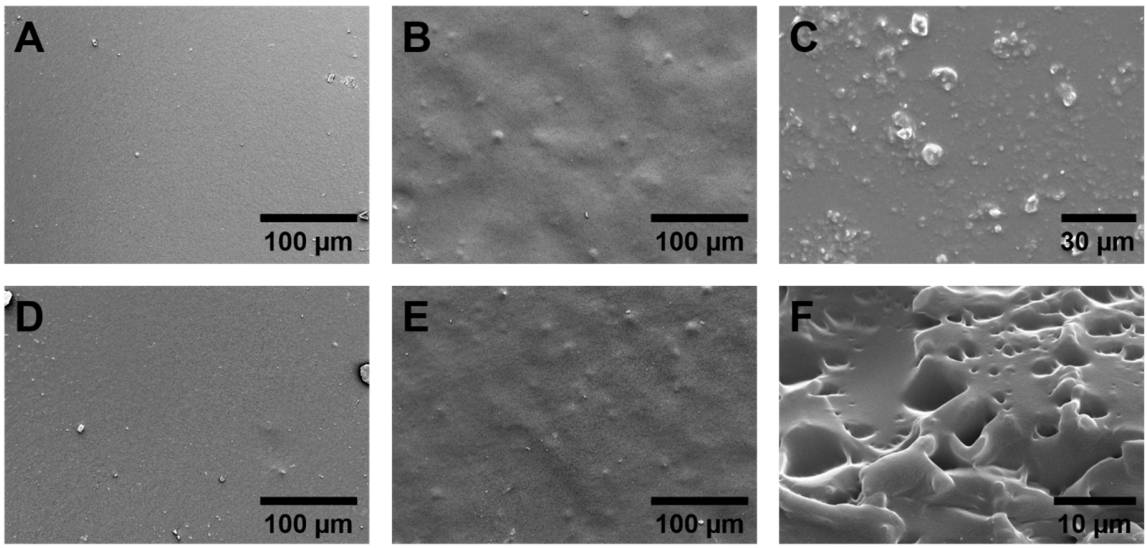

Fig. S6 Scanning electron microscopy (SEM) images showing the surface of PGSG specimens after degradation. (A-C) PGSG10 incubated for 28 days at 37 °C in (A) PBS only, (B) lipase + PBS, and (C) collagenase + PBS. (D-F) PGSG20 incubated for 28 days at 37 °C in (D) PBS only, (E) lipase + PBS, and (F) collagenase + PBS.

Proof-of-concept fabrication of PGSG20 tissue scaffolds

The fabrication was conducted by a combined technique of salt-leaching and freeze-drying. Salt from a local store was sieved doubly to obtain sizes of 300 µm and mixed with the molten PGSG20 pre-polymer resin at a weight ratio of 3:1 at 65 °C by mechanical stirring (100 rpm) for 15 min. The mixture was then cast into a PTFE petri dish and placed in a vacuum oven at 120 °C for 24 h to cure the pre-polymer. Next, the cured sample was immersed in 0%, 30%, 70%, and 100% water-ethanol solutions at 40 °C for 3 days, during which the salt particles were washed-out by diffusion to create macro-pores in the scaffold whilst the scaffold became fully swollen. Finally, this swollen scaffold was placed in a freeze dryer (FreeZone Triad Freeze Dry System, Labconco) to remove water and create additional micro-pores in order to improve the pore interconnectivity.[10] The freeze-drying cycle consisted of a pre-freezing stage at -40 °C overnight followed by drying at -10 °C for 24 h.

The mechanical property of PGSG20 scaffolds was determined by a compressive mechanical testing with a Hounsfield H100KS (Tinius Olsen). The disk-shaped specimens were prepared using a mould stencil (n = 6; diameter: 10 mm). A 10 N load cell was used at a compressive rate of 50 mm min^{-1}. SEM was also conducted to investigate the microscopic pore structures (Philips XL 30S FEG; spot size = 3, accelerating voltage = 10 kV). The cross-sectional area was examined after a gold-coating.

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